

# INSIGHTS INTO THE SULFUR MINERALOGY OF MARTIAN SOIL AT ROCKNEST, GALE CRATER, ENABLED BY EVOLVED GAS ANALYSES.

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**Introduction:** The first solid samples analysed by the Chemistry and Mineralogy (CheMin) instrument and Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) consisted of < 150  $\mu\text{m}$  fines sieved from aeolian bedform material at a site named Rocknest. All four samples of this material analyzed by SAM's evolved gas analysis mass spectrometry (EGA-MS) released  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{SO}_2$  (Fig. 1), as well as  $\text{H}_2\text{S}$  and possibly  $\text{NO}$ . This is the first time evolved  $\text{SO}_2$  (and evolved  $\text{H}_2\text{S}$ ) has been detected from thermal analysis of martian materials. The identity of these evolved gases and temperature (T) of evolution can support mineral detection by CheMin and place constraints on trace volatile-bearing phases present below the CheMin detection limit or difficult to characterize with XRD (e.g., X-ray amorphous phases). Constraints on phases responsible for evolved  $\text{CO}_2$  and  $\text{O}_2$  are detailed elsewhere [1,2,3]. Here, we focus on potential constraints on phases that

terize analog samples under SAM-like conditions (flight SAM-like carrier gas, gas flow and gas pressure conditions, T range and heating ramp rate). Several milligrams of <150  $\mu\text{m}$  samples were analyzed.

**Rocknest evolved  $\text{SO}_2$ :** The intensity and shape of traces attributable to  $\text{SO}_2$  (Fig. 1) vary substantially between the Rocknest samples. This likely indicates heterogeneity in sulfur minerals or phases which can evolve  $\text{SO}_2$  or their abundances, as well as possibly differences in other sample components that play a role in oven reactions that can produce  $\text{SO}_2$ . Overall, however,  $\text{SO}_2$  traces have a hump indicating  $\text{SO}_2$  evolving from ~450 to ~800°C. Within this, at least two “peaks” can be deconvolved, one with peak Ts at ~500-550°C, and one with peak Ts at ~700-750°C (Fig. 1).

Evolved  $\text{SO}_2$  could result from a range of potential sources. It could result from S anions adsorbed onto sample materials, or thermal decomposition of S-bearing mineral phases including sulfides, sulfates, and/or sulfites. Data from SAM-like EGA-MS analyses of several S-bearing phase reference materials are shown in Fig. 2 for preliminary comparisons to Rocknest data, although work to build SAM-like EGA-MS reference libraries is ongoing. As shown in Fig. 2, Mg- and Ca-sulfates have  $\text{SO}_2$  evolution Ts which are probably too high to be responsible for Rocknest  $\text{SO}_2$  (Ca-sulfates evolve  $\text{SO}_2$  at >1000 °C). Heating of a reduced S phase in the presence of an oxidant (e.g.,  $\text{CO}_2$ ,  $\text{O}_2$ ), and/or  $\text{SO}_2$  from other reactions between S-phases and other sample volatile-bearing phases during heating are another possibility. In addition, differences in  $\text{SO}_2$  evolution Ts due to particle size differences in S-bearing phases, and other sources which remain to be determined, are potential contributions.

It is also relevant to note that more than one  $\text{SO}_2$  peak may result even from only one sulfide mineral in a sample, depending on which other gases are in the oven and how reducing or oxidizing the oven atmosphere is at certain Ts. To investigate this idea, mixtures of minor pyrite in calcite were prepared, and then analyzed in SAM-like EGA lab setups. Several of these analyses produced  $\text{SO}_2$  traces with two peaks. A mixture of minor pyrite in nontronite showed similar

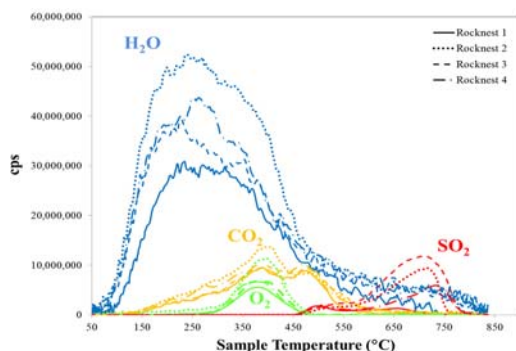


Figure 1. Major gases evolved from Rocknest soil fines during MSL SAM EGA-MS. Lines are plots of MS signal vs. temperature for the major molecular ion for a given compound. Figure by H. Franz.

evolved  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{O}$  during thermal analysis.

**Methods:** For SAM EGA-MS analyses, delivered sample fines were heated to ~835°C at 35°C/min. Evolved gases were carried through manifold lines to the SAM QMS by a He carrier gas. The pressure of He in the oven was ~30 mb and the flow rate was ~1.4 cc/min. The SAM breadboard and other SAM-like EGA teststands at GSFC and JSC were used to charac-

features, and future work is planned with other mineral mixtures. We hypothesize that some  $\text{SO}_2$  is from partial oxidation of the pyrite-hosted reduced S, and then remaining reduced S, possibly in a pyrrhotite reaction product, is then oxidized at the higher Ts by  $\text{CO}_2$  or  $\text{H}_2\text{O}$  in the oven at that T. EGA analyses of the minor pyrite mixtures also show a peak in the 60 Da trace, which can be attributed to OCS. Reaction of  $\text{CO}_2$  with a reduced S phase can result in an OCS product [4].

In Rocknest data, there is a 60 Da peak that correlates with the higher T  $\text{SO}_2$  release (Fig. 3). There is no large  $\text{CO}_2$  release at that T, but some residual  $\text{CO}_2$  is present. There is also evolution of species at 34, (Fig. 3), 35, and 36 Da (not shown) contemporaneous but not exactly correlated with the higher T  $\text{SO}_2$  peak (Fig. 3). We hypothesize that these high T species are due to  $\text{H}_2\text{S}$  release, and SAM GCMS data from several Rocknest samples indicates  $\text{H}_2\text{S}$ . The 34 Da peak at lower T can be primarily attributed to an isotopologue of  $\text{O}_2$  (Fig. 1), though GCMS data indicates that minor  $\text{H}_2\text{S}$  must also be present at the lower T and work is on going. Species at 76 Da contemporaneous with the higher T  $\text{SO}_2$  may indicate  $\text{CS}_2$  evolution (not shown).  $\text{CS}_2$ , like OCS, may also be a reaction product of a reduced S phase and oven volatiles. The presence of  $\text{H}_2\text{S}$  supports the idea that reduced S was still present in the sample at the time of the highest T  $\text{SO}_2$  peak.

**Rocknest evolved  $\text{H}_2\text{O}$ :** The shape of the  $\text{H}_2\text{O}$  traces are similar between the Rocknest samples (Fig. 1), though the intensity of the low T  $\text{H}_2\text{O}$  hump varies. There are many possible sources of the relatively large amount of water released at  $<500^\circ\text{C}$ , as well as for the lower  $\text{H}_2\text{O}$  signal at higher Ts. Adsorbed  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  bound to x-ray amorphous phases (e.g., amorphous aluminosilicate materials, nanophase ferric oxides/oxhydroxides) or interlayer  $\text{H}_2\text{O}$  from expandable phyllosilicates, could contribute to the lower T water, as could the dehydration of several salts (e.g. sulfate phases (Fig. 4)), though the lack of CheMin detection of phyllosilicates or hydrated sulfates suggests that any water from those potential sources is comparatively minor. Higher T  $\text{H}_2\text{O}$  could be due to more tightly bound structural  $\text{H}_2\text{O}$  and OH in minor minerals present below the CheMin detection limit (e.g., from some phyllosilicates), as well as  $\text{H}_2\text{O}$  occluded in minerals (e.g., fluid inclusions in sulfate salts).

**Discussion:** To date, no sulfides or sulfates other than minor anhydrite have been detected by CheMin [5]. This implies their abundance is  $<1\text{-}2\text{ wt. \%}$ . Another consideration is that  $\text{SO}_2$  could be evolved from X-ray amorphous materials (e.g., sulfate-adsorbed allophane shown in Fig. 2, X-ray amorphous sulfates, etc.). The presence of S-bearing phases is also indicated by APXS analyses of bulk Rocknest soil [6].

Even small amounts of sulfates in soil fines at Gale indicate some aqueous alteration, and could be relevant to the potential for preservation of any organic compounds. Sulfides can be indicative of comparatively reducing conditions, and in general more reducing environments are better for organic preservation. The possibility of both reduced and oxidized sulfur compounds together in the Rocknest soils may play a key part in unraveling the provenance of the soil fines.

## References:

- [1] Sutter et al. (2013a) *LPSC XLIV*. [2] Sutter et al. (2013b) *LPSC XLIV*. [3] Archer et al. (2013) *LPSC XLIV*. [4] Bhargava et al. (2009) *Fuel*, 88, 988. [5] Bish et al. (2013) *LPSC XLIV*. [6] Morris et al. (2013) *LPSC XLIV*.

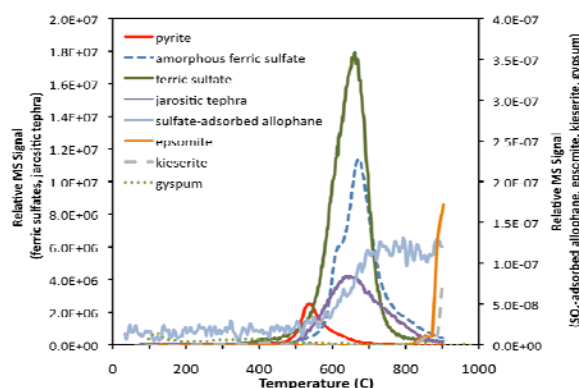


Figure 2. SAM-like EGA-MS  $\text{SO}_2$  traces from several sulfur phase reference materials, for comparison with Rocknest data.

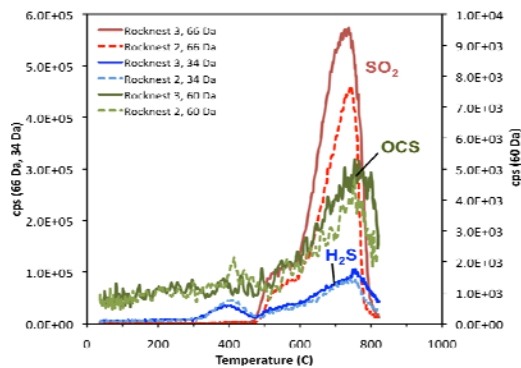


Figure 3. Representative SAM EGA-MS traces attributable to  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and OCS from Rocknest sample analyses.

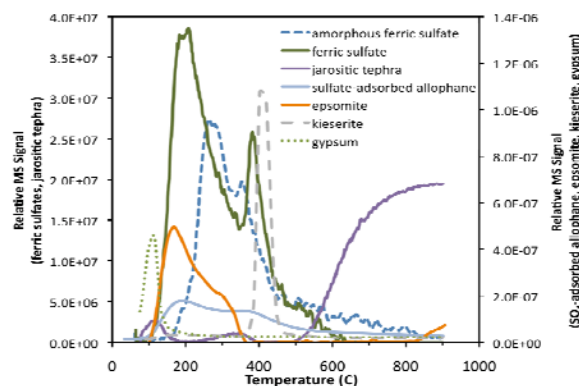


Figure 4. SAM-like EGA-MS  $\text{H}_2\text{O}$  traces from several sulfur phase reference materials, for comparison with Rocknest data.